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Synthesis of Fluorosulfates and Difluorophosphates by the Heterolytic Cleavage of Polysulfuryl Fluorides and Pyrophosphoryl Fluoride with 2-Substituted Perfluoroisopropoxide and Fluoroalkoxide Anions

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The reactions between perfluorohalogenoidohydrin and perfluoroalkoxide salts and pyrosulfuryl difluoride and trisulfuryl difluoride as well as pyrophosphoryl tetrafluoride lead to fluorosulfate and difluorophosphate esters. The syntheses and physical properties of the new compounds 2-cyano-2-O-fluorosulfatohexafluoropropane, 2-thiocyanato-2-O-fluorosulfatohexafluoropropane, and 2-isothiocyanato-2-O-fluorosulfatohexafluoropropane are described.

The compound 2-cyano-2-O-fluorosulfatohexafluoropropane, $(CF_3)_2C(CN)OSO_2F$, and the isomers 2-thiocyanato- and 2-isothiocyanato-2-O-fluorosulfatohexafluoropropane, $(CF_3)_2C(SCN)OSO_2F$ and $(CF_3)_2C(NCS)OSO_2F$, respectively, are the first examples of O-fluorosulfates with a halogenoid group on the geminal carbon. The method of preparation, *e.g.*, involves the nucleophilic displacement of a fluorosulfate anion from pyrosulfuryl fluoride by an isopropoxide anion

$$(CF_3)_2C(X)O^- + S_2O_5F_2 \longrightarrow (CF_3)_2C(X)OSO_2F + SO_3F^-$$

where X = CN, SCN, or NCS. This is a new procedure for the synthesis of fluoroalkyl fluorosulfate esters. The trifluoromethoxide ion can also be employed, and trisulfuryl fluoride may be substituted for pyrosulfuryl fluoride.

Precedent for this type of reaction has been established by Ruff, who found that hard bases like F^- ion or borderline bases like Cl^- or N_3^- ions would heterolytically cleave pyrosulfuryl fluoride to give derivatives such as FSO_2F, FSO_2Cl, and FSO_2N_3, whereas soft nucleophiles like Br^- or CN^- give Br_2 and $(CN)_2$, respectively, along with SO_2F_2 and SO_2.[1]

These same 2-halogenoidoperfluoroisopropoxide ligands have been used to prepare fluorophosphine, fluorophosphate, and fluorothiophosphate esters by the displacement of bromide from the appropriate phosphorus bromide difluoride.[2] However, in the analogous reaction between sulfuryl bromide fluoride and the cyanohydrin salt, no fluorosulfate ester could be isolated under similar conditions. To further illustrate the displacement reactions of the halogenoidohydrin anions of hexafluoroacetone, the cyano and azido derivatives can displace the difluorophosphate anion from pyrophosphoryl fluoride, *i.e.*

$$(CF_3)_2C(X)O^- + P_2O_3F_4 \longrightarrow (CF_3)_2C(X)OP(O)F_2 + PO_2F_2^-$$

where X = CN or N_3. This reaction is similar to that reported by Roesky[3] and provides an alternate course for the synthesis of fluorophosphate esters. It should be noted that there has been no report of the isolation of perfluorohalogenoidohydrin salts other than $Na^+(CF_3)_2C(CN)O^-$, but evidence for the corresponding thiocyanato-, isothiocyanato-, and azidohydrin salts as reaction intermediates has been established in this work as well as in another recent report.[2]

Experimental Section

Reagents.—Pyrosulfuryl fluoride, trisulfuryl fluoride, and pyrophosphoryl fluoride were prepared by the literature methods.[4-6] Sodium 2-cyanoperfluoroisopropoxide was synthesized by the addition of hexafluoroacetone (HFA) to sodium cyanide.[7] Sodium trifluoromethoxide was prepared by the method of Redwood and Willis.[8] The sodium cyanide, thiocyanate, and azide salts and HFA were obtained from the General Chemical Division of Allied Chemical Corp. The salts were dried by pumping *in vacuo* at 100° for 4 hr and used without further purification.

General Technique and Analytical and Spectral Instrumentation.—All volatile chemicals were manipulated within a standard Pyrex apparatus. Otherwise, materials were handled in a drybox with a nitrogen atmosphere. The reactor was a 100-ml Pyrex bulb with a Fischer-Porter Teflon valve for an inlet and containing a Teflon-coated stirring bar. Carbon and nitrogen in the samples were analyzed by combustion using an F & M Model 185 analyzer. Fluorine was determined by reduction of the compounds with lithium in *n*-propylamine. Molecular weights by vapor density measurements were obtained assuming perfect gas behavior using a 208.2-ml Pyrex bulb. Vapor pressure measurements were obtained by the method of Foord.[9] Temperatures of the samples in the apparatus were controlled using a water bath. Cathetometers were used for the measurement of pressure indicated by a mercury manometer and for observing the null point of the spoon gauge. Melting points were observed by placing samples contained in 5-mm o.d. Pyrex tubes into a dewar flask with an unsilvered strip and using a pentane cold bath. All new compounds have been characterized by elemental analyses and spectroscopic measurements as well as by other physical data. Previously prepared compounds have been identified by their spectra and molecular weight determinations.

Infrared spectra were taken with a Perkin-Elmer 621 grating infrared spectrometer or with an Infracord spectrometer using a 10-cm path length gas cell with cesium bromide windows at pressures <15 mm. The ^{19}F nmr spectra were taken using a Varian Model V4310 spectrometer operating at 40 Mc. Samples were measured at room temperature in 5-mm o.d. Pyrex tubes using CCl_3F as an internal standard. A Consolidated Engineering Corp. Model 61-620 spectrometer with a heated inlet system and operating at 100 eV was used to obtain mass spectra.

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[7] W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **32**, 951 (1967).

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TABLE I

OTHER REACTIONS

Substrate[a]	Reactant[a]	Time, min	Solvent (vol)	Products[a]
$CsOCF_3$ (6.5)	$S_2O_5F_2$ (0.62)	5	Nitromethane (2 ml)	CF_3OSO_2F (0.20), SO_2F_2 (0.45), COF_2 (0.36), CO_2 (0.05)
$Na^+(CF_3)_2C(CN)O^-$ (0.65)	SO_2BrF (0.65)	5	Nitrobenzene (1 ml)	SO_2[b]
$Na^+(CF_3)_2C(CN)O^-$ (4.1)	$P_2O_3F_4$ (4.2)	10	Nitrobenzene (2 ml)	$(CF_3)_2C(CN)OP(O)F_2$ (4.0), POF_3 (trace), $NaPO_2F_2$[c]
$Na^+(CF_3)_2C(N_3)O^-$ [d] (2.7)	$P_2O_3F_4$ (2.8)	30	Nitrobenzene (1.5 ml)	$(CF_3)_2C(N_3)PO(O)F_2$ (2.2), POF_3 (small amount), $(CF_3)_2CO$, $NaPO_2F_2$[c]

[a] The numbers in parentheses are millimoles of substrate, reactants, and products. [b] Sulfur dioxide was the major product and no fluorosulfate ester was detected. [c] Identified by its infrared spectrum. [d] Prepared *in situ* by stirring NaN_3 (2.7) and HFA (3.0) in nitrobenzene for 24 hr.

Synthesis of $(CF_3)_2C(CN)OSO_2F$.—Nitrobenzene (1 ml) and $Na^+(CF_3)_2C(CN)O^-$ (0.825 mmol) were charged into the reactor, and then an equimolar amount of $S_2O_5F_2$ was added into the reactor at −196°. The mixture was warmed over a 15-min period to ambient temperature and then stirred for an additional 5 min. The products were passed through cold traps set at −45 and −80°. The former held the nitrobenzene; the trap at −80° held the pure product (0.82 mmol, essentially quantitative yield). The solid left in the reactor was $NaSO_3F$ according to infrared identification. Alternately, $(CF_3)_2C(CN)OSO_2F$ was prepared by adding trisulfuryl fluoride, $S_3O_8F_2$ (1.34 mmol), to an equimolar amount of the sodium cyanohydrin salt in the presence of 1 ml of nitrobenzene at −196°, and the above procedure was repeated. The recovery was 0.52 mmol of the fluorosulfate ester (39% yield). Final purification was accomplished by passage through a 10-ft FC-43 on Chromosorb P chromatographic column at 75°. The retention time was 12.6 min at a 60-cm^3/min helium flow rate. *Anal.* Calcd for $C_4F_7NO_3S$: C, 17.33; F, 48.01; N, 5.05. Found: C, 17.42; F, 48.4; N, 5.00. The molecular weight was 270.0 g/gram molecular volume (calcd, 275.1). The compound melts at −63.0 ± 0.5°.

The mass spectral cracking pattern recorded as mass number (assumed species) and relative abundance is as follows: 12 (C^+) 0.3, 14 (N^+) 0.2, 16 (O^+) 0.2, 26 (CN^+) 0.5, 28 (CO^+) 1.2, 31 (CF^+) 4.8, 32 (S^+, O_2^+) 0.6, 48 (SO^+) 2.2, 50 (CF_2^+) 1.7, 54 ($COCN^+$) 5.3, 57 ($CFCN^+$) 0.4, 64 (SO_2^+) 2.0, 69 (CF_3^+) 100.0, 70 ($^{13}CF_3^+$) 1.3, 76 (CF_2CN^+) 0.8, 80 (SO_3^+) 0.7, 83 (SO_2F^+) 16.0, 85 ($^{34}SO_3F^+$) 0.8, 88 (CF_4^+) 0.4, 97 ($C_2F_3O^+$) 8.7, 104 ($C_2F_2OCN^+$) 1.9, 119 ($C_2F_5^+$) 0.9, 128 ($C_3F_4O^+$) 0.2, 147 ($C_3F_5O^+$) 0.2, 206 ($C_2F_3OSO_2FCN^+$) 0.2, 249 ($C_3F_{10}OSO_2F^+$) 0.2.

Some of the observed vapor pressures at various temperatures for $(CF_3)_2C(CN)OSO_2F$ are: −10.9°, 5.3 mm; −5.2°, 27.1 mm; 6.2°, 50.9 mm; 21.1°, 102.9 mm; 31.9°, 159.2 mm; 37.8°, 199.6 mm; 43.1°, 246.9 mm; 47.0°, 287.0 mm. The vapor pressure measurements follow the Clausius–Clapeyron equation $\log P_{mm} = 7.236 - (1629/T)$. The latent heat of vaporization is 7.454 kcal/mol and the Trouton constant is 22.83 eu.

Synthesis of the Isomers $(CF_3)_2C(SCN)OSO_2F$ and $(CF_3)_2C(NCS)OSO_2F$.—These compounds were prepared by the addition of excess HFA (12.2 mmol) to NaSCN (10.0 mmol) in 2 ml of nitrobenzene and stirring for 24 hr. Then $S_2O_5F_2$ (5.47 mmol) was added into the reactor. The mixture was stirred for 0.5 hr and passed through traps at −45°, −95, and −196°. The nitrobenzene was retained in the −45° trap while the isomeric mixture (2.1 mmol, 38% yield) was held in the −95° trap and HFA, SO_2, and SO_2F_2 were found in the trap at −196°. *Anal.* Calcd for $C_4F_7NO_3S_2$: C, 15.64; F, 43.30; N, 4.56. Found: C, 15.35; F, 42.9; N, 4.25. The molecular weight was 312 (calcd, 307). Although the distillation and chromatographic methods used could not achieve the separation of the isomers, $(CF_3)_2C(NCS)OSO_2F$ appears to have the lesser volatility.

Other reactions performed in a similar manner and at 25° are given in Table I.

Results and Discussion

The reactions between some 2-halogenoidoperfluoroisopropoxide and trifluoromethoxide anions and polysulfuryl fluorides have produced fluorosulfates in generally good yield. When $CsOCF_3$ was used as a substrate with $S_2O_5F_2$, substantial quantities of COF_2 and SO_2F_2 were formed, although CF_3OSO_2F was also produced. These results may be explained by the sequence

$$CF_3O^- + S_2O_5F_2 \longrightarrow CF_3OSO_2F + SO_3F^-$$

$$CF_3O^- \rightleftharpoons COF_2 + F^-$$

$$F^- + CF_3OSO_2F \longrightarrow SO_2F_2 + CF_3O^-$$

The work included in this report as well as that by Ruff[1] demonstrates the generality of the method as well as the limitations. A further example of a limitation is provided by the reaction between $Na^+(CF_3)_2C(CN)O^-$ and sulfuryl bromide fluoride. Instead of a simple displacement of bromide ion and formation of a fluorosulfate, SO_2 is a major product. However, this result, nevertheless, could be predicted,[1] although a fluorophosphate does result by the reaction between the same anion and POF_2Br.[2]

The infrared spectra of the new compounds are consistent with the formulations given. The spectrum of $(CF_3)_2C(CN)OSO_2F$ shows a weak and broad band at 2252 cm^{-1}, assigned to the C≡N stretching frequency.[2,10] The absorption at 1480 cm^{-1} (ms) is attributed to the asymmetric S═O stretching motion of the fluorosulfate group and that due to the symmetric stretch is presumed to be part of the very strong, broad, and complex band centered at 1250 cm^{-1},[11] which is assigned to a C—F stretching motion. Other bands in the region generally associated with C—F and C—O stretching vibrations are at 1293 (s), 1115 (ms), 1050 (s), and 970 cm^{-1} (ms). The S–F stretching modes are assigned to the absorptions at 855 (s) and 829 cm^{-1} (ms),[11] while the band associated with the S—O stretching vibration is located at 725 cm^{-1} (m).[11] Unassigned absorptions are at 667 (m), 600 (ms), 542 (m), 485 (w), and 440 cm^{-1} (vw).

Although the thiocyanato and isothiocyanato mixture could not be separated into the pure components, sufficient separation could be achieved to allow some tentative infrared absorption band assignments. Comparison can be made with the corresponding fluoro-

(10) J. H. Simons, *Fluorine Chem.*, **2**, 483 (1954).
(11) M. Lustig and J. K. Ruff, *Inorg. Chem.*, **4**, 1441 (1965).

phosphate esters.[2] The frequency presumed to be associated with the asymmetric stretching vibration of the isothiocyanato group is assigned to the band at 1905 cm^{-1} (vs), while that due to the thiocyanato group is at 1972 cm^{-1} (vs).[12,13] A band of smaller intensity also occurs at 2041 cm^{-1} in the spectrum of the latter. The corresponding frequencies in the spectra of the fluorophosphate derivatives are shifted *ca.* 100 cm^{-1} to higher frequency.[2] The asymmetric S═O stretching frequency in both esters is centered at 1471 cm^{-1} (s). The symmetric S═O absorption is obscured by the very strong band assigned to the C—F stretching frequency at *ca.* 1250 cm^{-1} (b). These compounds have other bands in the region associated with C—F stretching motions at 1193 (s), 1107 (w) [isothiocyanato isomer], 1047 (m), 1019 (ms), and 970 cm^{-1} (s). Bands tentatively assigned to S–F stretching modes are at 866 (vs) and 826 cm^{-1} (vs). Those assigned to S—O stretching modes are at 724 cm^{-1} (m) [thiocyanato isomer] and 687 cm^{-1} (ms) [isothiocyanato (?)]. Other absorptions are at 922 (w) and 885 cm^{-1} (sh).

Also diagnostic are the ^{19}F nmr spectra of these compounds. The spectrum of $(CF_3)_2C(CN)OSO_2F$ shows a resonance absorption at ϕ -47.9 (septuplet, J_{F_6-F} = 2.5 cps) and a doublet centered at ϕ 73.7 (J_{F_6-F} = 2.5 cps). Homo decoupling can convert either multiplet into a singlet. The area ratio of the high-field resonance to that at low field was measured to be 6.1:1.0, and, therefore, the low-field multiplet is assigned to the S–F fluorine resonance,[11] and that at high field to the six equivalent nuclei of the fluorine atoms bound to the carbon atoms. The isomeric mixture $(CF_3)_2C(SCN)OSO_2F$ and $(CF_3)_2C(NCS)OSO_2F$ shows S–F fluorine resonances at ϕ -48.9 and -47.7 and C–F fluorine resonances at ϕ 78.7 and 81.3.

The mass spectra of these compounds show complicated patterns. The spectrum of the thio- and isothiocyanato mixture was not included in the Experimental Section, but fragment ions containing the SCN moiety are abundant. A parent peak (P^+) at m/e = 307 is present and a high-intensity absorption at mass number 58 corresponding to SCN^+ is observed. The fluorophosphate analogs also exhibit a high-intensity absorption at this latter mass number corresponding to the same species. This is unusual because all of the other perfluoroorganohalogenoidohydrin fluorophosphate and fluorosulfate compounds show low-intensity absorptions at mass numbers associated with the halogenoid group. The compounds prepared in this work also show absorptions due to the fluorocarbon and/or fluorosulfate fragments.

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Preparation and Properties of Methyltellurium Trichloride. Factors Affecting the State of Aggregation of Group VI Halides and Organohalides

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The preparation of previously unknown methyltellurium trichloride is reported. Methyltellurium trichloride is a colorless crystalline solid, soluble in benzene and methylene chloride. Thermal stability increases in the series $CH_3SCl_3 < CH_3SeCl_3 < CH_3TeCl_3$. Cryoscopic studies in benzene show an increasing order of polymerization with $CH_3TeCl_3 < CH_3SeCl_3 < CH_3TeBr_3$. For the first time a unifying theory is presented which rationalizes the interesting range of structures and the solution behavior of organochalcogen(IV) and chalcogen(IV) halides.

Methylchalcogen(IV) halides of the general formula $(CH_3)_nMX_{4-n}$ (where M = S, Se, Te; X = F, Cl, Br, I; and n = 1, 2, 3) have been the subject of a number of recent studies.[1-4] These compounds are of particular interest because the interpretation of various spectroscopic studies is relatively straightforward, compared to corresponding derivatives with more complicated organo substituents. It was therefore of interest to prepare the previously unreported methyltellurium trichloride in order to compare its properties to those of methyltellurium tribromide[3] and methylselenium trichloride[2] and tribromide. The results of our study are reported below.

Experimental Section

General Information.—The atmospheric moisture sensitivity of the compounds used in this study necessitated handling these materials *in vacuo* or in dry nitrogen filled glove bags.

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(3) M. Chen and J. W. George, *ibid.*, **90**, 4580 (1968).

(4) K. J. Wynne and J. Puckett, *Chem. Commun.*, 1532 (1968).